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Note

Magnetic and thermal characterization of $Na_2NiP_2O_7$ crystals

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Abstract : $Na_2NiP_2O_7$ crystals were synthesized by hydrothermal technique and characterized by DTA/TGA, XRD, FTIR and measured magnetic property. $Na_2NiP_2O_7$ crystals are crystallized in monoclinic system. DTA/TGA results revealed a phase transition at 524°C and magnetically, it is a frequency-dependent paramagnetic material and the thermal treatment to the material has resulted in change of magnetic properties from paramagnetic to ferrimagnetic.

Keywords : Hydrothermal synthesis, pyrophosphates, DTA/TGA, XRD, magnetism.

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The study of alkali transitional metal phosphates has drawn significant attention owing to their wide synergetic properties and applications as prospective materials in technology, *viz.*, in electronic device and as solid electrolyte with high thermal resistance, a potential device in space application, sensors, laser materials, piezoelectric, luminescence, ceramics and magnetic materials, *etc.* [1–6]. The magnetic susceptibility measurement of phosphates has attracted great attention since last few decades because of its potential applications in field sensing and magnetic recording heads and its improved performance for opto-electronic devices [7–9]. Recently, the authors have reported a series of phosphates, which exhibited tunnel type of framework structures with open cavities and have shown good electrical and magnetic properties [10–12]. Here, we report a new group of phosphates, which seems to be prospective magnetic materials with relatively high thermal stability.

The synthesis experiments were carried out by earlier reported hydrothermal route at moderate temperature and pressure conditions [11,12]. The reagents used are of analar grade of NaOH (99.99%), H_3PO_4 (98%) and $NiCl_2$ (99%) from Glaxo chemicals without further purification. Initially, NaOH and H_3PO_4 were taken in a teflon-lined Morey type autoclave with capacity of 50 ml. Later, a known quantity of nickel chloride of known molar concentration was added to it and thoroughly stirred till homogeneity was attained. The pH of starting reactant was 4.18. The crystallization was carried out by spontaneous nucleation and the rate of nucleation was controlled through programmed slow rate of heating (5–10°C/h). The experiments were carried out for 10 days continuously at temperature range of 250–260°C and pressure of 60–100 bars followed by sudden quenching to the ambient conditions. The resultant product was thoroughly washed with distilled water using ultrasonic cleaner and pH of the resultant product was 3.29. $Na_2NiP_2O_7$ crystals are obtained under the following molar ratios :

$$Na_2O : NiO : P_2O_5 :: 2–4 : 1.5–2.5 : 10–12.$$

Successful growth of technologically important phosphate crystals in the form of single crystals will depend on several growth parameters. In the case of hydrothermal synthesis, the most important growth parameters are selection of starting reactants, suitable solvent, percent fill, temperature, pressure, *etc.* Among them, the selection of the reactant materials and the solvent is the most important aspect. In the present experiment, H_3PO_4 and

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NaOH solutions have been used as the solvents and nickel chloride as solute. The linkage between the solvent and solute is essentially of coordination type and hence, various acid-base complexes have been observed in solution. It is easy to understand the acid-base complex formation in simple systems. But it is difficult in a multi-component system like the one discussed in the present work, consisting of more than four components. Therefore, understanding of the formation of such a coordination compound is extremely difficult. However, on the basis of pH conditions of chemical reactions prevailed in the initial (4.18) and resultant products (3.29), it has changed from acidic to relatively stronger acidic conditions. Based on these results, the following reactions have been proposed :

$$NiCl_2 + H_3PO_4 \rightarrow NiHPO_4 + 2HCl \rightarrow 1,$$

$$2NaOH + H_3PO_4 \rightarrow HNa_2PO_4 + 2H_2O \rightarrow 2,$$

$$NiHPO_4 + HNa_2PO_4 \rightarrow Na_2NiP_2O_7 + H_2O \rightarrow 3.$$

The crystals obtained by this method were of good quality with well-developed faces : {100}, {210} and {001}. On the whole, the crystals exhibited smooth surface morphology, sub-vitreous luster, green colour and having a size of 2.0–2.5 mm (Figure 1).

X-ray diffraction (XRD) :

X-ray studies have been carried out by Rigaka Miniflex diffractometer with graphite monochromatized $CuK\alpha$ radiation (λ = 1.5405 Å) in steps of 0.02° at room temperature (Figure 2) The cell parameters and the volumes were calculated by using the software programme, 'The Crysfire 2002 system for automatic powder indexing and user's manual' [13] and the results are given in Table 1.

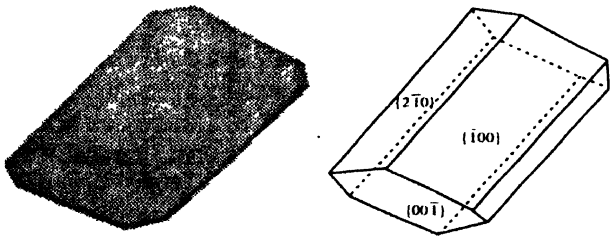

Figure 1. CCD photograph and schematic diagram of $Na_2NiP_2O_7$ crystal.

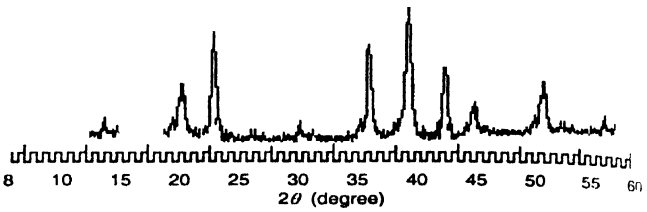

Figure 2. Powder XRD pattern of $Na_2NiP_2O_7$ crystal.

DTA/TGA :

The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of $Na_2NiP_2O_7$ have been recorded by using TGA 7 Perkin Elmer, US analyzer in the temperature range of 55–800°C under the oxygen atmosphere. The heating rate used for the analysis was 10°C/minute. The diagram clearly exhibited large weight loss at 524°C (Figure 3). The weight loss at 524°C is due to the endothermic irreversible phase transition. This compound exhibited relatively high thermal stability.

FTIR-spectrum :

FTIR-Spectrum was recorded using a high resolution Perkin Elmer Infrared Spectrophotometer, in the range of 4000–400 cm^{-1} (Figure 4). The compound exhibits prominent multiple absorption bands especially in three frequency regions *i.e.* at ν_1 (2312.3 cm^{-1}), ν_2 (1211.2–952.8 cm^{-1}) and ν_3 (723.3–461 cm^{-1}). The vibrations at ν_1 is due to the Ni-O-Ni bonding, ν_2 and ν_3 are due to the presence of P-O-P bonding. The degree of multiplication and fineness in the spectrum of phosphates increases as the degree of polymerization increases in the $[PO_4]$ tetrahedral [10–12]. It is clearly noticed that the

Table 1. Powder XRD data of $Na_2NiP_2O_7$.

Number of lines		Mean Absolute discrepancies		Max. Error accepted	Figures of merit	
Input data = 18	Calculated = 190	Q = 1429E–03	$\Delta(2\theta)$ = 1736E–01,	(Deg.2θ) = 4500E–01	$M(18)$ = 5.3	$F(18)$ = 5.5, (0.0174, 190)
Standard deviations			0.0053	0.0082	0.0042	0.038
Cell parameters		a = 10.1543		b = 9.9819	c = 9.9053Å	
		β = 96.684°		V = 997.17 Å^3	Monoclinic system	

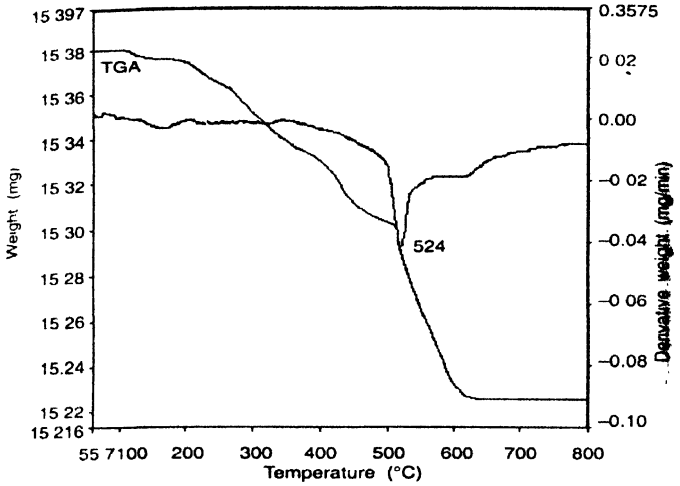

Figure 3. DTA/TGA curve of $Na_2NiP_2O_7$ compound.

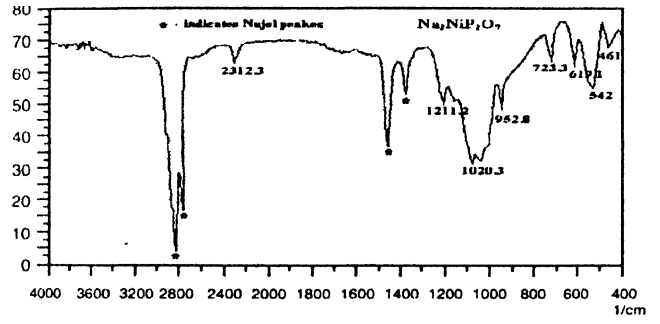

Figure 4 FTIR spectrum of $Na_2NiP_2O_7$ compound.

compound has exhibited more number of splittings and high degree of sharpness especially in the low frequency regions indicating condensation of $[PO_4]^{3-}$ tetrahedral to $[P_2O_7]^{4-}$. This result is supported by the X-ray results. No vibrations are noticed at 3600–3000 cm^{-1} indicating absences of hydrate molecules.

Magnetic susceptibility :

Magnetic susceptibility measurements were made using Gouy balance method by applying field strengths of 0.5–3.0 K Gauss at 300 K (Figure 5). Magnetic moments of the compound show paramagnetic behavior. In general, nickel derivatives fall into two broad classes; Nickel(II) derivatives have two unpaired electrons either high spin octahedral with μ_{eff} in the range of 2.81–3.93 BM or low spin octahedral with lesser μ_{eff} (<2.83 BM) [14,15]. In the present work, $Na_2NiP_2O_7$ materials have shown magnetic moments in the range of 1.54–2.34 BM. These values are much lower than those reported for nickel derivatives with low spin octahedral. It could be attributed

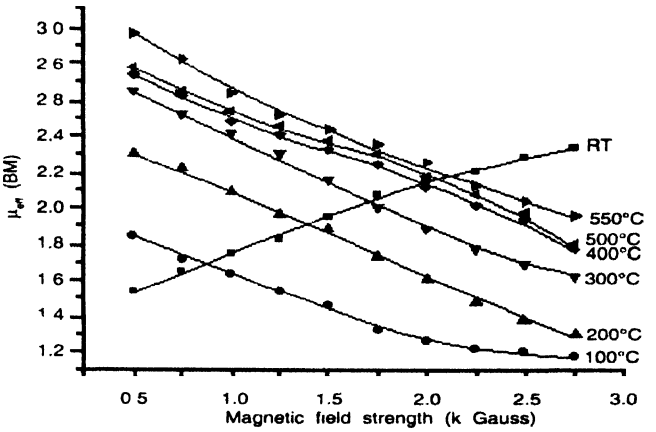

Figure 5. Magnetic moment vs magnetic field strength of $Na_2NiP_2O_7$ compound at various temperature.

to the bonding of diamagnetic phosphorus ion with the paramagnetic nickel ion through the common oxygen ion (P-O-Ni) in the structure. Here, nickel derivatives of sodium-bearing phosphates have positive correlation with magnetic moment. To unravel the thermal effect on the magnetic properties, the material has been subjected to heat treatments for an hour at 100, 200, 300, 400, 500 and 550°C followed by DTA/TGA studies. After the thermal treatment, magnetic susceptibility measurements were made and the corresponding μ_{eff} values were calculated. The μ_{eff} results of the thermally-treated materials have shown negative correlation with the magnetic field strength. It has been attributed to the fact that the heat treatment could have changed the behavior of the materials from paramagnetic to ferrimagnetic and resulted in a negative correlation with the magnetic field strength.

$Na_2NiP_2O_7$ crystals were synthesized by hydrothermal method in the form of single crystals with well-developed morphology. DTA/TGA studies revealed that the material has relatively high thermal stability. The XRD studies have shown, that it is crystallized in monoclinic system. It is also a frequency-dependent paramagnetic material and has a positive correlation with the magnetic field strength. However, the thermal treatment to the material has resulted in a change in the magnetic properties from paramagnetic to ferrimagnetic and μ_{eff} has exhibited negative correlation with the magnetic field strength.

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